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A combined first principles and analytical determination of the modulus of cohesion, surface energy, and the additional constants in the second strain gradient elasticity

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ABSTRACT

Mindlin's (1965) second strain gradient theory due to its competency in capturing the effects of edges, corners, and surfaces is of particular interest. Formulation in this framework, in addition to the usual Lamé constants, requires the knowledge of sixteen additional materials constants. To date, there are no successful experimental techniques for measuring these material parameters which reflect the discrete nature of matter. The present work gives an accurate remedy for the atomistic calculations of these parameters by utilizing the first principles density functional theory (DFT) for the calculations of the atomic force constants combined with an analytical formulation. It will be shown that writing the consistency conditions obtained from the equivalency between the atomistic crystal lattice dynamics of the bulk material and its counterpart in the second strain gradient elasticity is insufficient for the calculations of all the additional constants. As it will be discussed, there are two missing conditions which are then provided by consideration of the free standing film problem that bring the surface effect into account. As a consequence of surface effect consideration, the modulus of cohesion which is one of the important additional constants is calculated. Moreover, an analytical expression for the surface energy in terms of the modulus of cohesion, Lamé constants, materials characteristic lengths, and the film thickness is presented. If the film thickness is much bigger than the magnitude of the characteristic lengths of the material, then the surface energy would no longer depend on the film thickness.

1. Introduction

Inadequacy of the traditional continuum theories in treating such problems as surface effects, nano-size defects, and stress concentrations, suggests to resort to augmented continuum theories as a remedy. The materials characteristic lengths or internal length scales which are on the atomic scale reflect the discrete nature of matters but are absent in the formulations within traditional continuum theories; on the other hand, it is due to the appearance of these characteristic lengths in the formulations within augmented continuum frameworks that makes them suitable not only for capturing certain size dependent effects, but also for enhancing the accuracy of the solutions as well. Following the work of Voigt (1887, 1894), an early higher order continuum theory was first introduced by Cosserat brothers (Cosserat and Cosserat, 1909) in which in addition to three translational degrees of freedom for each material point, three rotational degrees of freedom are also incorporated. Toupin (1964) incorporated eighteen components of the first gradient of the strain tensor into the potential energy density of the elastic continuum. An interesting phenomenon is the surface effect which becomes remarkably important for nano-sized structures with very large surface-to-volume ratio. Mindlin's second strain gradient theory given for centrosymmetric materials is an early higher order continuum theory which can account for the surface effects among other phenomena (Mindlin, 1965). He considered a homogeneous, isotropic, and centrosymmetric material and derived the linear equations of equilibrium, constitutive relations, and conditions for the edges, corners, and surfaces. In the Mindlin's second strain gradient theory, the potential energy density of the material is assumed to be a second degree polynomial consisting of all the possible quadratic terms obtained from: any combination of six components of the infinitesimal strain field, eighteen components of the first gradient of the strain tensor, and thirty components of the second gradient of the strain tensor. In addition, to account for the modulus of cohesion, Mindlin introduces a linear term involving the second gradient of strain into the potential energy density. This additional term which gives rise to the self-equilibrating components of cohesive force, as it will be seen, results in nonzero fourth-order stress tensor, even if the displacement field is identically equal to zero.

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Depending on the utilized higher order continuum theory to account for the nano- and micro-structure of materials, it is natural to inquire more in-depth knowledge of material parameters and characteristics in addition to just the Lamé constants. For example, Mindlin's first strain gradient elasticity involves five additional constants, and Mindlin's second strain gradient theory requires sixteen additional constants. It is noteworthy to mention that among these sixteen constants, there is a parameter that stands for cohesion and is referred to as the modulus of cohesion. In the present work, an analytical expression for the surface energy is derived in terms of the modulus of cohesion as well as other additional constants in the second strain gradient framework. As it will be seen, if the modulus of cohesion is zero, then the surface energy vanishes.

To date, the experimental determination of the additional parameters or material internal length scale(s) has encountered with great obstacles. Due to the lack of experimental and computational data on these material properties, quantitative analyses based on these enriched theories have been impossible. DiVincenzo (1986) developed an analytical procedure based on the higher-order theory of continuum elasticity to capture the dispersive nature of the propagation of phonons with wavelengths in the mesoscopic scale (neither macroscopic nor microscopic). The starting point of the work of DiVincenzo is consideration of a special continuum Lagrangian density which is quadratic with respect to the displacement field, $\mathbf{u}$; the subsequent analysis is then within the harmonic approximation. More specifically, the considered Lagrangian expression excludes some of the quadratic terms, namely the quadratic form of the type $\left(\partial^3 u_i/\partial x_j\partial x_k\partial x_l\right)\left(\partial^3 u_m/\partial x_n\partial x_p\partial x_q\right)$ which for isotropic materials gives rise to seven terms; here $\partial/\partial x_i$ denotes the spatial derivative with respect to x_i. In fact, among all the quadratic terms involving the second strain gradient (highest strain gradient considered), DiVincenzo maintains only the quadratics of the type $\left(\partial u_i/\partial x_j\right)\left(\partial^3 u_m/\partial x_n\partial x_p\partial x_q\right)$. The Lagrangian density defined in this manner served the purposes for the study undertaken by DiVincenzo (1986), dispersive effects in the acoustic phonons in crystalline GaAs. This form for Lagrangian is neither pertinent to the first strain gradient elasticity nor to the second strain gradient elasticity. In fact, none of the available higher order continuum theories which have been developed for the purposes of capturing the size effect, surface effects, dispersive nature of waves in media with microstructure, or nanoscopic studies near defects are governed with the Lagrangian used by DiVincenzo. Maranganti and Sharma (2007) utilized the same Lagrangian density to obtain the so-called "dynamic elastic constants" (involving fourth-, fifth-, and sixth-order elasticity constants) rather than the explicit calculation of the gradient constants (coefficients) appearing in the Lagrangian expression. In contrast, the present work aims to calculate the modulus of cohesion and the additional constants in the Mindlin's second gradient elasticity explicitly. Danescu (2012) and Danescu and Grenet (2012) have employed the discrete valence force field model to evaluate the mentioned dispersive dynamic elastic constants for diamond-like crystals. Charlotte and Truskinovsky (2008), based on writing the displacement field as two-scale decomposition (macro- and micro-deformations) proposed by Eringen (1968), developed a multi-scale continuum elasticity theory for the linear elastic behavior of crystal lattices. In this framework, they afforded to reduce the strongly nonlocal problem to a nested set of second order differential equations. Recently, Shodja and Tehranchi (2010, 2012) and Shodja et al. (2012) proposed an analytical formulation for the calculation of the characteristic lengths of fcc materials, respectively, in the first and second strain gradient elasticity using a many-body long-range Finnis–Sinclair potential (Finnis and Sinclair, 1984); the parameters of the predefined potential which describes the interatomic interactions, are determined based on either empirical data or electronic structure calculations. Typically, the full interactions are broken up into two-body, three-body, and many-body contributions, long-range and short-range terms and so on. These contributions and terms have no theoretical background, casting doubts on reliability in approximation and accuracy of parameters of concern.

With the aid of the milestone basic theory of Hohenberg and Kohn (1964) and Kohn and Sham (1965), and subsequent developments, however, it has been feasible, at least in principle, to exactly represent the properties of a stationary many-particle system, despite its complex nature, without recourse to the Schrödinger equation and from a variational principle involving only the electronic density. The only approximation in the Kohn–Sham equations (Kohn and Sham, 1965) of density functional theory (DFT) is due to calculation of the exchange and correlation energy which is most commonly expressed as local density approximation (LDA) and its improved form of generalized gradient approximation (GGA). Thus, regarding the tractability and acceptable accuracy of the computational procedures based on DFT, it is made possible to achieve a reliable estimation for macroscopic characteristics such as elastic moduli tensors and surface energy. Ojaghnezhad and Shodja (2012) employed ab initio calculations based on DFT to evaluate the bulk elastic moduli tensors of order four and six for crystalline silicon of diamond structure. Moreover, they computed the surface properties such as surface energy, surface stress, and surface elastic moduli tensor for ideal and reconstructed surfaces of Si(001). The methodology for the determination of the bulk and surface elastic moduli tensors is based upon the calculation of the Helmholtz free energy of the crystal which is subjected to appropriate modes of uniform strain loadings. Delfani et al. (2013) employed the same methodology to evaluate the fourth and sixth order elastic moduli tensors of graphene as well as the longitudinal Young's modulus of achiral single wall carbon nanotubes. In spite of the efficiency of the mentioned method in evaluation of the elastic moduli tensors pertinent to both the linear and nonlinear terms of the constitutive relation within the traditional continuum elasticity, it becomes inoperative for the current purposes of obtaining the higher order elastic tensors which correspond to the gradients of the strain tensor. Recently, Shodja et al. (2013) proposed an analytical formulation to link the elastic constants of the first strain gradient elasticity to the components of the Hessian matrix of the potential energy; the elements of the Hessian matrix are obtained via ab initio DFT and subsequently, the first strain gradient characteristic lengths for some fcc and bcc metal crystals are calculated. In present work, however, the remedy is to come up with the consistency equations stemming from the equivalency between the atomistic crystal dynamics expressed in terms of atomic force constants and the corresponding dynamics in the second strain gradient elasticity framework. To this end, the dynamics of mass points located on a space lattice of crystals is considered. Subsequently, the elements of the Hessian matrix of the potential energy (or equivalently the atomic force constants) are related to the corresponding components of the elastic moduli tensors. However, employing the above-mentioned remedy to the bulk is not sufficient for calculating all the additional constants involved in the second strain gradient elasticity. In fact, consideration of the bulk alone can at best lead to the determination of only some components of the higher order elastic moduli tensors, while some other components remain unknown. As it will be seen, the encountered dilemma is a manifestation of two missing consistency conditions. The missing equations are discussed by considering a free standing film problem for which surface effect is important. It should be emphasized that the calculation of the modulus of cohesion which is one of the important additional parameters is not possible without consideration of the surface effects. Moreover, in the study of surface characterization, a surface characteristic length is defined.

The paper is organized as below. Section 2 includes the theories and formulations due to the second strain gradient theory and

lattice dynamics (described in Sections 2.1 and 2.2, respectively) as well as the linkage between these theories (explained in Section 2.3). The surface embodiment of the second strain gradient elasticity is extracted in Section 3 through applying the theory to the infinitely extended and free standing film of the finite thickness. Section 4 is devoted to the first principles calculations for the case study Al. In this section, the atomic force constants of the bulk Al together with the surface characteristics of the thin film Al(001) (including surface energy and change in the film thickness) are computed using the ab initio calculations based on DFT. Combining the numerical first principles results with the formerly derived relations based on lattice dynamics and second strain gradient theory, the Lamé and additional constants of Al are evaluated.

2. Theory and formulations

2.1. Second strain gradient theory

Mindlin (1965) developed the second gradient theory of elasticity wherein the change in the potential energy per initial undeformed volume of the elastic continuum (called strain energy density) is written in terms of the classic infinitesimal strain components, ϵ_{ij} as well as ϵ_{ijk} and ϵ_{ijkl} which are the second and third gradients of displacement field u_i defined as below

$$\epsilon_{ij} = \frac{1}{2}\left(u_{i,j} + u_{j,i}\right), \tag{1a}$$

$$\epsilon_{ijk} = u_{k,ij}, \tag{1b}$$

$$\epsilon_{ijkl} = u_{l,ijk}, \tag{1c}$$

where $u_{i,j}$ denotes the partial differentiation of the i^{th} component of the displacement field, u_i with respect to the j^{th} component of the Cartesian coordinate, x_j. The higher rank tensors ϵ_{ijk} and ϵ_{ijkl} with eighteen and thirty independent components, respectively, can be replaced by the strain first and second gradients.

According to Mindlin (1965), for a homogeneous, centrosymmetric, and isotropic material, the most general form of the second degree polynomial strain energy density, W has the following form

$$\begin{aligned} W = &\frac{1}{2}\lambda\epsilon_{ii}\epsilon_{jj} + \mu\epsilon_{ij}\epsilon_{ij} + a_1\epsilon_{ijj}\epsilon_{ikk} + a_2\epsilon_{iik}\epsilon_{kjj} + a_3\epsilon_{iik}\epsilon_{jjk} \\ &+ a_4\epsilon_{ijk}\epsilon_{ijk} + a_5\epsilon_{ijk}\epsilon_{kji} + b_1\epsilon_{iijj}\epsilon_{kkll} + b_2\epsilon_{ijkk}\epsilon_{ijll} + b_3\epsilon_{iijk}\epsilon_{jkll} \\ &+ b_4\epsilon_{iijk}\epsilon_{llkj} + b_5\epsilon_{iijk}\epsilon_{lljk} + b_6\epsilon_{ijkl}\epsilon_{ijkl} + b_7\epsilon_{ijkl}\epsilon_{jkli} + c_1\epsilon_{ii}\epsilon_{jjkk} \\ &+ c_2\epsilon_{ij}\epsilon_{ijkk} + c_3\epsilon_{ij}\epsilon_{kkij} + b_o\epsilon_{iijj}, \end{aligned} \tag{2}$$

in which λ and μ are the classic Lamé constants, and the a_i's, b_i's, c_i's, and b_0 are the additional material constants. For hyperelastic materials, the constitutive equations for isotropic elastic continuum in the second gradient theory are written as below

$$\begin{aligned} \tau_{pq} = \frac{\partial W}{\partial \epsilon_{pq}} &= \lambda\epsilon_{ii}\delta_{pq} + 2\mu\epsilon_{pq} + c_1\epsilon_{iijj}\delta_{pq} + c_2\epsilon_{pqii} \\ &+ \frac{1}{2}c_3(\epsilon_{iipq} + \epsilon_{iiqp}), \end{aligned} \tag{3a}$$

$$\begin{aligned} \tau_{pqr} = \frac{\partial W}{\partial \epsilon_{pqr}} &= a_1(\epsilon_{pii}\delta_{qr} + \epsilon_{qii}\delta_{pr}) \\ &+ \frac{1}{2}a_2(\epsilon_{iip}\delta_{qr} + 2\epsilon_{rii}\delta_{qp} + \epsilon_{iiq}\delta_{pr}) \\ &+ 2a_3\epsilon_{iir}\delta_{pq} + 2a_4\epsilon_{pqr} + a_5(\epsilon_{rqp} + \epsilon_{rpq}), \end{aligned} \tag{3b}$$

$$\begin{aligned} \tau_{pqrs} = \frac{\partial W}{\partial \epsilon_{pqrs}} &= \frac{2}{3}b_1\epsilon_{iijj}\delta_{pqrs} + \frac{2}{3}b_2\epsilon_{jkii}\delta_{jkpqrs} \\ &+ \frac{1}{6}b_3\left[(\epsilon_{iikj} + \epsilon_{iijk})\delta_{jkpqrs} + 2\epsilon_{jsii}\delta_{jpqr}\right] \\ &+ \frac{2}{3}b_4\epsilon_{iisj}\delta_{jpqr} + \frac{2}{3}b_5\epsilon_{iijs}\delta_{jpqr} + 2b_6\epsilon_{pqrs} \\ &+ \frac{2}{3}b_7(\epsilon_{qrsp} + \epsilon_{rspq} + \epsilon_{spqr}) + \frac{1}{3}c_1\epsilon_{ii}\delta_{pqrs} + \frac{1}{3}c_2\epsilon_{ij}\delta_{ijpqrs} \\ &+ \frac{1}{3}c_3\epsilon_{is}\delta_{ipqr} + \frac{1}{3}b_o\delta_{pqrs}, \end{aligned} \tag{3c}$$

in which τ_{pq} is the traditional Cauchy stress tensor, and τ_{pqr} and τ_{pqrs} are the components of the higher order stress tensors, δ_{ij} is the Kronecker-delta, and

$$\delta_{ijkl} = \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}, \tag{4a}$$

$$\delta_{ijklmn} = \delta_{ik}\delta_{jl}\delta_{mn} + \delta_{ik}\delta_{jm}\delta_{ln} + \delta_{il}\delta_{jm}\delta_{kn}. \tag{4b}$$

The stress formulation for the equations of motion of the elastic medium has been obtained to be

$$\tau_{ji,j} - \tau_{jki,jk} + \tau_{jkli,jkl} + f_i = \rho\ddot{u}_i, \tag{5}$$

where f_i is the body force and ρ is the mass density of the material.

It is observed that there are eighteen material parameters in the second gradient framework including the usual Lamé constants. Lamé constants have been evaluated via both experimental and theoretical methods. As discussed in the introduction section, the second strain gradient theory is particularly useful to account for the surface effects. As it will be shown, the parameter b_0 is directly related to the surface energy. The aim of the current work is to provide a quantum based remedy for the calculation of the additional parameters including b_0.

2.2. Atomistic manifestation of the equations of motion

In this section, the atomistic formulation of the energy density and equations of motion of the atom in perfect crystal associated with the second gradient theory of strain is introduced. In subsequent sections, the second gradient parameters are evaluated by linking the derived formulation with the ab initio calculations.

Consider an infinitely extended crystal of perfect lattice periodicity for which the primitive lattice vectors are denoted by $\mathbf{v}_1, \mathbf{v}_2$, and $\mathbf{v}_3$. To avoid lengthy manipulations, the crystals with single-atomic basis in the primitive unit cell are discussed. Assume that the index vector $\mathbf{l} = (l_1, l_2, l_3)$, where l_1, l_2, and l_3 are integers, is employed to identify the primitive unit cells of the crystal. Then, the equilibrium position of the atom in the unit cell $\mathbf{l} = (l_1, l_2, l_3)$ is denoted by

$$\mathbf{a}^{(\mathbf{l})} = l_1\mathbf{v}_1 + l_2\mathbf{v}_2 + l_3\mathbf{v}_3. \tag{6}$$

Due to the atomic fluctuations (displacements), $\mathbf{u}^{(\mathbf{l})}$, the final position of each atom, $\mathbf{r}^{(\mathbf{l})}$ is deviated from its equilibrium position through the following relation

$$\mathbf{r}^{(\mathbf{l})} = \mathbf{a}^{(\mathbf{l})} + \mathbf{u}^{(\mathbf{l})}. \tag{7}$$

The crystal potential energy, E depends on the instantaneous position of atoms and can be expanded with respect to the variables $\mathbf{u}^{(\mathbf{l})}$ as follows

$$\begin{aligned} E = (E)_{\mathbf{u}^{(\mathbf{l})}=0} &+ \sum_{\mathbf{l}}\left(\frac{\partial E}{\partial u_i^{(\mathbf{l})}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} u_i^{(\mathbf{l})} \\ &+ \frac{1}{2}\sum_{\mathbf{l},\mathbf{l}'}\left(\frac{\partial^2 E}{\partial u_i^{(\mathbf{l})}\partial u_j^{(\mathbf{l}')}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} u_i^{(\mathbf{l})}u_j^{(\mathbf{l}')}, \end{aligned} \tag{8}$$

where $E_0 = (E)_{\mathbf{u}^{(\mathbf{l})}=0}$ is the energy of the system at equilibrium state. In the above expansion, the higher order terms are omitted and hence the obtained results would correspond to the harmonic approximation of the problem. The i-component of the conservative force acting on the atom $\mathbf{l}$ is written as

$$F_i^{(\mathbf{l})} = -\frac{\partial E}{\partial u_i^{(\mathbf{l})}} = -\left(\frac{\partial E}{\partial u_i^{(\mathbf{l})}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} - \sum_{\mathbf{l}'}\left(\frac{\partial^2 E}{\partial u_i^{(\mathbf{l})}\partial u_j^{(\mathbf{l}')}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} u_j^{(\mathbf{l}')}. \tag{9}$$

In the equilibrium state, the resultant of the forces acting on each atom of the crystal is equal to zero, hence

$$\left(\frac{\partial E}{\partial u_i^{(\mathbf{l})}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} = 0, \tag{10}$$

and therefore, within the harmonic approximation, the change of the potential energy with respect to the equilibrium state is expressed as below

$$\Delta E = \frac{1}{2}\sum_{\mathbf{l},\mathbf{l}'}\left(\frac{\partial^2 E}{\partial u_i^{(\mathbf{l})}\partial u_j^{(\mathbf{l}')}}\right)_{\mathbf{u}^{(\mathbf{l})}=0} u_i^{(\mathbf{l})}u_j^{(\mathbf{l}')}. \tag{11}$$

Considering Eqs. (9) and (10), one can deduce the following expression for the equations of motion of the atom $\mathbf{l}=\mathbf{0}$

$$m\ddot{u}_i^{(\mathbf{0})} = -\sum_{\mathbf{l}} U_{ij}^{(\mathbf{0},\mathbf{l})}u_j^{(\mathbf{l})}, \tag{12}$$

in which m is the mass of the atom in the crystal and $U_{ij}^{(\mathbf{0},\mathbf{l})}$ is referred to as the atomic force constant defined using the following relation

$$U_{ij}^{(\mathbf{l},\mathbf{l}')} = \left(\frac{\partial^2 E}{\partial u_i^{(\mathbf{l})}\partial u_j^{(\mathbf{l}')}}\right)_{\mathbf{u}^{(\mathbf{l})}=0}. \tag{13}$$

It is readily inferred that $U_{ij}^{(\mathbf{l},\mathbf{l}')}$ is equal to the negative force exerted in the i-direction on the atom $\mathbf{l}$ when the atom $\mathbf{l}'$ has a unit displacement in the j-direction.

Now, define a spatially slowly-varying displacement field $\mathbf{u}(\mathbf{x})$ which is equal to $\mathbf{u}^{(\mathbf{l})}$ at the lattice site $\mathbf{a}^{(\mathbf{l})}$. Writing the Taylor's series expansion for $\mathbf{u}^{(\mathbf{l})}$ about $\mathbf{l}=\mathbf{0}$ results in

$$\begin{aligned} u_j^{(\mathbf{l})} &= u_j^{(\mathbf{0})} + u^0_{j,k}a_k^{(\mathbf{l})} + \frac{1}{2}u^0_{j,kl}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})} + \frac{1}{6}u^0_{j,klm}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})} \\ &\quad + \frac{1}{24}u^0_{j,klmn}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})} + \frac{1}{120}u^0_{j,klmnp}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})} \\ &\quad + \frac{1}{720}u^0_{j,klmnpq}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})}a_q^{(\mathbf{l})}, \end{aligned} \tag{14}$$

where

$$u^0_{j,k\ldots l} = \left(\frac{\partial^s u_j}{\partial x_k \ldots \partial x_l}\right)_{\mathbf{x}=\mathbf{0}}, \quad s = 1,\ldots,6. \tag{15}$$

In above relation, $\mathbf{x}$ is the position variable. By substituting Eq. (14) into Eq. (12), it is concluded that

$$\begin{aligned} m\ddot{u}_i^{(\mathbf{0})} &= -u_j^{(\mathbf{0})}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})} - u^0_{j,k}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})} - \frac{1}{2}u^0_{j,kl}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})} \\ &\quad - \frac{1}{6}u^0_{j,klm}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})} \\ &\quad - \frac{1}{24}u^0_{j,klmn}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})} \\ &\quad - \frac{1}{120}u^0_{j,klmnp}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})} \\ &\quad - \frac{1}{720}u^0_{j,klmnpq}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})}a_q^{(\mathbf{l})}. \end{aligned} \tag{16}$$

It is well known that if the crystal is subjected to an arbitrary rigid body motion, the inertia term associated with each atom would equal zero. Therefore, Eq. (12) results in

$$\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})} = 0. \tag{17}$$

Moreover, based on the translational symmetry of crystals with respect to their lattice vectors, the following identity holds (Born and Huang, 1954; Brüesch, 1982)

$$U_{ij}^{(\mathbf{l},\mathbf{l}')} = U_{ij}^{(\mathbf{l}-\mathbf{l}',\mathbf{0})} = U_{ij}^{(\mathbf{0},\mathbf{l}'-\mathbf{l})}. \tag{18}$$

Additionally, each atom in the perfect centrosymmetric crystal of infinite extent is at an inversion center which implies

$$U_{ij}^{(\mathbf{0},\mathbf{l}-\mathbf{l}')} = U_{ij}^{(\mathbf{0},\mathbf{l}'-\mathbf{l})}. \tag{19}$$

Employing the above-mentioned identities, the following relations are inferred

$$\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})} = 0, \tag{20a}$$

$$\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})} = 0, \tag{20b}$$

$$\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})} = 0. \tag{20c}$$

By considering Eqs. (17) and (20), and letting $m=\rho V$, where ρ is the mass density and V is the volume of the primitive unit cell, then the equation of the motion (16) may be written as

$$\rho\ddot{u}_i^{(\mathbf{0})} = \widetilde{C}_{ijkl}u^0_{j,kl} + \widetilde{C}_{ijklmn}u^0_{j,klmn} + \widetilde{C}_{ijklmnpq}u^0_{j,klmnpq}, \tag{21}$$

in which

$$\widetilde{C}_{ijkl} = -\frac{1}{2V}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}, \tag{22a}$$

$$\widetilde{C}_{ijklmn} = -\frac{1}{24V}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}, \tag{22b}$$

$$\widetilde{C}_{ijklmnpq} = -\frac{1}{720V}\sum_{\mathbf{l}}U_{ij}^{(\mathbf{0},\mathbf{l})}a_k^{(\mathbf{l})}a_l^{(\mathbf{l})}a_m^{(\mathbf{l})}a_n^{(\mathbf{l})}a_p^{(\mathbf{l})}a_q^{(\mathbf{l})}. \tag{22c}$$

From the definition of the atomic force constants, Eq. (13), it is readily deduced that

$$U_{ij}^{(\mathbf{l},\mathbf{l}')} = U_{ji}^{(\mathbf{l}',\mathbf{l})}. \tag{23}$$

Utilizing the relations (18) and (23) together with the definitions (22), it is concluded that the above-defined tensors are symmetric with respect to indices i and j. The additional symmetries are due to the interchange of $a_k^{(\mathbf{l})}$ to $a_q^{(\mathbf{l})}$. Moreover, it can be shown that $\widetilde{C}_{ijkl} = \widetilde{C}_{klij}$ (Brüesch, 1982). According to the mentioned symmetries, the tensors $\widetilde{C}_{ijkl}$, $\widetilde{C}_{ijklmn}$, and $\widetilde{C}_{ijklmnpq}$ consist of 21, 90, and 168 independent elements, respectively. Using ab initio based on DFT, all the elements are evaluated as described in Section 4. It is necessary to note that for crystals which are non-primitive and have more than one atom in their primitive unit cells, the assumption that every atom is at a center of inversion would not be correct in general, and hence the corresponding simplifications can not be applied. In this case, the expressions for $\widetilde{C}_{ijkl}, \widetilde{C}_{ijklmn}$, and $\widetilde{C}_{ijklmnpq}$ would become very complex. However, despite the complexity, the proposed methodology can be extended to multi-component materials.

2.3. Relating the Lamé and additional constants to the atomic force constants

The objective of this section is to relate the Lamé constants as well as the additional parameters to the atomic force constants which are computed using ab initio calculations. To this end, it is necessary to express the equation of motion, in the second strain gradient framework, in terms of the displacement field in a form analogous to the equation of motion (21) which is based on the crystal lattice dynamics.

Generally speaking, the strain energy density function associated with solids, without regard to any specific symmetry, in the context of the second strain gradient theory may be expressed as

$$\begin{aligned} W &= \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl} + F_{ijklmn}\epsilon_{ij}\epsilon_{klmn} + \frac{1}{2}G_{ijklmn}\epsilon_{ijk}\epsilon_{lmn} \\ &\quad + \frac{1}{2}I_{ijklmnpq}\epsilon_{ijkl}\epsilon_{mnpq} + B^{\circ}_{ijkl}\epsilon_{ijkl}. \end{aligned} \tag{24}$$

Assuming hyperelastic material, the corresponding stress tensors are given by

$$\tau_{ij} = C_{ijkl}\epsilon_{kl} + F_{ijklmn}\epsilon_{klmn}, \tag{25a}$$
$$\tau_{ijk} = G_{ijklmn}\epsilon_{lmn}, \tag{25b}$$
$$\tau_{ijkl} = F_{pqijkl}\epsilon_{pq} + I_{ijklmntu}\epsilon_{mntu} + B^{\circ}_{ijkl}, \tag{25c}$$

where $B^{\circ}_{ijkl} = \frac{b_0}{3}\delta_{ijkl}$. Utilizing the above relations together with the symmetry considerations of the strain and stress tensors, it is inferred that the fourth, sixth, and eighth order tensors, respectively, C_{ijkl}, F_{ijklmn}, G_{ijklmn}, and $I_{ijklmntu}$ have the following symmetry properties

$$C_{ijkl} = C_{klij} = C_{jikl} = C_{ijlk}, \tag{26a}$$
$$F_{ijklmn} = F_{jiklmn} = F_{ijlkmn} = F_{ijmlkn} = F_{ijkmln}, \tag{26b}$$
$$G_{ijklmn} = G_{lmnijk} = G_{jiklmn} = G_{ijkmln}, \tag{26c}$$
$$I_{ijklmnrs} = I_{mnrsijkl} = I_{jiklmnrs} = I_{kjilmnrs} = I_{ijlkmnrs} = I_{ijklrnms} = I_{ijklnmrs} = I_{ijklmrns}. \tag{26d}$$

Employing the above-mentioned symmetry relations and by comparing Eqs. (24) and (25), respectively, with Eqs. (2) and (3), the nonzero components of the tensors $\mathbf{C}, \mathbf{F}, \mathbf{G}$, and $\mathbf{I}$ are obtained in terms of the Lamé and additional constants for isotropic materials. Recall that, for the fourth order elastic moduli tensor $C_{1111} = \lambda + 2\mu$, $C_{1122} = \lambda$, and $C_{1212} = \mu$. The relations between the higher order tensors, F_{ijklmn}, G_{ijklmn}, and $I_{ijklmnpq}$ and the additional constants, a_i's, b_i's, and c_i's are summarized in Tables 1 and 2. The other nonzero components (not found in the tables) can be obtained through the cyclic permutation of indices of the displayed components.

Substituting the strain and stress components from Eqs. (1) and (25), into the stress formulation of equations of motion (5) results in

$$\rho\ddot{u}_i = C_{jikl}u_{k,lj} + \left(F_{pqjkli} + F_{liqjkp} - G_{klijqp}\right)u_{p,qjkl} + I_{jklimnrs}u_{s,mnrjkl}. \tag{27}$$

The comparison between Eq. (27) with its atomistic counterpart (21) reveals that

$$C_{imjn} = \widetilde{C}_{ijmn} + \widetilde{C}_{mjin} - \widetilde{C}_{mijn}, \tag{28a}$$
$$2\widetilde{C}_{ijmnpq} = F_{jmnpqi} + F_{jnmpqi} + 2F_{qimnpj} - 2G_{pqimnj}, \tag{28b}$$
$$2\widetilde{C}_{ijmnpqst} = I_{qstimnpj} + I_{mstiqnpj}. \tag{28c}$$

Hence, the components of the elastic tensors $\mathbf{C}, \mathbf{F}, \mathbf{G}$, and $\mathbf{I}$ are related to the components of $\tilde{\mathbf{C}}$ which in turn are related to the atomic force constants, $U_{ij}^{(\mathbf{0},\mathbf{l})}$ via Eqs. (22).

By combining Eqs. (28) with the relations provided in Tables 1 and 2, the Lamé constants and additional parameters are interconnected to the components of $\tilde{\mathbf{C}}$. The symmetry considerations of the components of $\tilde{\mathbf{C}}$ reduce the number of independent additional parameters to five through the following conditions

$$a_1 = a_2 = a_5, \tag{29a}$$
$$a_4 = 2a_3, \tag{29b}$$
$$c_3 = c_2 = 2c_1, \tag{29c}$$
$$4b_1 = 2b_2 = b_3 = 4b_4 = 4b_5 = 6b_6 = 2b_7. \tag{29d}$$

It is interesting to note that if the potential energy of the system is considered to be affected only by the change in the interatomic distances (which is due to the assumption of the central forces between the atoms), then $\widetilde{C}_{ijkl}$ is fully symmetric in all its indices; as a result $C_{ijkl} = \widetilde{C}_{ijkl}$. The full symmetry of $\widetilde{C}_{ijkl}$, in addition to the symmetries associated with those drawn from Eq. (22a), provides six more relations referred to as the Cauchy relations. Consequently, for a hyperelastic material with full symmetries of $\widetilde{C}_{ijkl}$, there are fifteen independent constants (Brüesch, 1982). For the materials with cubic symmetries, there are three independent constants, C_{1111}, C_{1122}, and C_{1212} which upon imposing the Cauchy relation, $C_{1122} = C_{1212}$ reduce to two independent constants. If the anisotropy ratio $AR = \frac{2C_{1212}}{C_{1111}-C_{1122}}$ defined for crystals with cubic symmetry is nearly equal to one, then the crystal is treated as isotropic and the pertinent Cauchy relation becomes $\lambda = C_{1122} = C_{1212} = \mu$. Note that Cauchy relation may not be valid for certain materials. For example, for isotropic materials we have that $\lambda = \frac{2\mu\nu}{1-2\nu}$, where ν is Poisson's ratio, and since for metals $\nu \approx 1/3$ it turns out that $\lambda \approx 2\mu$, and so Cauchy relation does not hold.

It should be emphasized that the relations between the fourth order elastic moduli tensor and Lamé constants as well as the relations between the higher order tensors and the additional constants provided in Tables 1 and 2 stem from the equation of the motion for the bulk, without any surface effects. It is noteworthy to mention that in all the above-mentioned relations the additional parameter b_0 is absent. This is not surprising since b_0 is not a parameter associated with the bulk. In fact, as it will be seen in the next section, b_0 characterizes the surface effects; moreover, a surface characteristic length, l_{10} will be revealed.

Table 2
The relations between the higher order tensor, $I_{ijklmnpq}$ and the additional constants, b_i's.

$I_{11111111} = \bar{b}$,	$I_{11111122} = I_{11111133} = \frac{2b_1+2b_2+b_3}{3}$,
$I_{11111221} = I_{11111331} = \frac{2b_1+b_3+2b_4+2b_5}{3}$,	$I_{11112222} = 2b_1$,
$I_{11122221} = 2b_4$,	$I_{11112233} = I_{11113322} = \frac{2b_1}{3}$,
$I_{11121112} = I_{11131113} = 2(b_5+b_6)$,	$I_{11121121} = I_{11131131} = \frac{b_3+2b_4+2b_7}{3}$,
$I_{11121222} = I_{11131333} = \frac{b_3+2b_5}{3}$,	$I_{11212331} = I_{11232333} = \frac{b_3+2b_5}{9}$,
$I_{11121233} = I_{11131232} = \frac{b_3}{6}$,	$I_{11121332} = I_{11131223} = \frac{2b_5}{3}$,
$I_{11122331} = I_{11133221} = \frac{2b_4}{3}$,	$I_{11211121} = I_{11311131} = \frac{2(2b_2+b_3+b_5+3b_6+2b_7)}{9}$,
$I_{11211222} = \frac{2(2b_2+b_3+b_4)}{9}$,	$I_{11211233} = I_{11311322} = \frac{4b_2+b_3}{18}$,
$I_{11211332} = I_{11311223} = \frac{b_3+2b_4}{9}$,	$I_{11221122} = I_{11331133} = \frac{2(b_1+b_2+b_4+b_5+3b_6+b_7)}{9}$,
$I_{11221133} = \frac{2(b_1+b_2)}{9}$,	$I_{11221221} = \frac{2(b_1+b_3+2b_7)}{9}$,
$I_{11221331} = I_{11331221} = \frac{2b_1+b_3}{9}$,	$I_{11222332} = \frac{2(b_1+b_4+b_5)}{9}$,
$I_{11231123} = I_{11321132} = \frac{2(b_5+3b_6)}{9}$,	$I_{11231132} = \frac{2(b_4+b_7)}{9}$,
$I_{11231231} = I_{11321231} = \frac{b_3+4b_7}{18}$,	$I_{12311231} = \frac{b_2+3b_6+b_7}{9}$.

3. Surface characteristic consideration

For examination of the role and involvement of the additional parameters in conveying the surface effects in the context of the second strain gradient elasticity, it is proposed to consider an infinitely extended free standing film of thickness, t. In the literature, surfaces are often considered as wall defects. Although, there is no

Table 1
The relations between the higher order tensors, F_{ijklmn} and G_{ijklmn} and the additional constants, a_i's and c_i's.

$F_{111122} = F_{111133} = \frac{c_1+c_2}{3}$,	$F_{111221} = F_{111331} = \frac{c_1+c_3}{3}$,	$F_{112222} = F_{113333} = c_1$,
$F_{112233} = F_{113322} = \frac{c_1}{3}$,	$F_{121112} = F_{131113} = \frac{c_3}{2}$,	$F_{121332} = F_{122331} = \frac{c_3}{6}$,
$F_{121121} = F_{131131} = \frac{c_2}{3} + \frac{c_3}{6}$,	$F_{111111} = c_1 + c_2 + c_3$,	$F_{121233} = \frac{c_2}{6}$,
$G_{112233} = G_{113322} = \frac{a_2}{2}$,	$G_{111122} = G_{111133} = \frac{2a_1+a_2}{2}$,	$G_{221111} = G_{331111} = a_2 + 2a_3$,
$G_{112112} = G_{113113} = 2(a_3 + a_4)$,	$G_{112211} = G_{113311} = \frac{a_2+2a_5}{2}$,	$G_{122122} = G_{133133} = \frac{a_1+2a_4+a_5}{2}$,
$G_{112332} = 2a_3$,	$G_{123123} = a_4$,	$G_{111111} = \bar{a}$,
$G_{122133} = \frac{a_1}{2}$,	$G_{123132} = \frac{a_5}{2}$.	

external loading applied to the film, it will undergo some deformations due to the surface effects. To obtain the displacement field for the problem of interest, by letting $\ddot{u}_i = 0$ in Eq. (5) and utilizing Eqs. (1) and (3), the equilibrium equation is written in terms of the displacement field as below

$$(\lambda+2\mu)\left(1-l_{11}^2\nabla^2\right)\left(1-l_{12}^2\nabla^2\right)u_{j,ji} - \mu\left(1-l_{21}^2\nabla^2\right)\left(1-l_{22}^2\nabla^2\right)e_{ijk}e_{kml}u_{l,mj}+f_i=0, \tag{30}$$

where e_{ijk} is the permutation tensor and

$$2(\lambda+2\mu)l_{1p}^2 = \bar{a}-2\bar{c}\pm\left[(\bar{a}-2\bar{c})^2-4\bar{b}(\lambda+2\mu)\right]^{\frac{1}{2}}, \tag{31a}$$

$$2\mu l_{2p}^2 = \bar{a}'-c_3\pm\left[(\bar{a}'-c_3)^2-4\bar{b}'\mu\right]^{\frac{1}{2}}, \tag{31b}$$

for $p=1$ and 2 pertinent to the positive and negative signs, respectively, and

$$\bar{a}=2(a_1+a_2+a_3+a_4+a_5), \tag{32a}$$

$$\bar{b}=2(b_1+b_2+b_3+b_4+b_5+b_6+b_7), \tag{32b}$$

$$\bar{c}=c_1+c_2+c_3, \tag{32c}$$

$$\bar{a}\prime=2(a_3+a_4), \tag{32d}$$

$$\bar{b}\prime=2(b_5+b_6). \tag{32e}$$

l_{11}, l_{12}, l_{21}, and l_{22} are the so-called "characteristic lengths" which are related to the Lamé and additional constants as given by Eqs. (31). It should be pointed out that when the characteristic lengths are identically equal to zero, Eq. (30) reduces to the traditional equation of equilibrium, which neglects the characteristic lengths. In continue, assuming that the characteristic lengths are nonzero, the deformation of the film due to the surface effects is examined next. Take the Cartesian coordinates in such a way that the x_1-axis is perpendicular to the free surfaces of the film ($x_1=\pm t/2$). Denoting the displacement component in the x_1-direction by $u_1(x_1)$, the equilibrium equation for the film becomes

$$l_{11}^2l_{12}^2\frac{d^6u_1}{dx_1^6}-\left(l_{11}^2+l_{12}^2\right)\frac{d^4u_1}{dx_1^4}+\frac{d^2u_1}{dx_1^2}=0. \tag{33}$$

The conditions on the film surfaces which are traction free imply that

$$\left[(\lambda+2\mu)u_{1,1}+(2\bar{c}-\bar{a})u_{1,111}+\bar{b}u_{1,11111}\right]_{x_1=\pm t/2}=0, \tag{34a}$$

$$\left[(\bar{a}-\bar{c})u_{1,11}-\bar{b}u_{1,1111}\right]_{x_1=\pm t/2}=0, \tag{34b}$$

$$\left[b_0+\bar{c}u_{1,1}+\bar{b}u_{1,111}\right]_{x_1=\pm t/2}=0. \tag{34c}$$

By considering condition (34a), the solution of the above equation becomes

$$u_1=C_1e^{\frac{x_1}{l_{11}}}+C_2e^{-\frac{x_1}{l_{11}}}+C_3e^{\frac{x_1}{l_{12}}}+C_4e^{-\frac{x_1}{l_{12}}}, \tag{35}$$

in which the rigid body displacement has been omitted. By satisfaction of the boundary conditions (34b) and (34c) and introducing the surface characteristic length, l_{10} as

$$l_{10}^2=\frac{\bar{c}}{\lambda+2\mu}, \tag{36}$$

the unknown coefficients are determined as

$$C_1=-C_2=-b_0l_{11}^2e^{t/(2l_{11})}\left(e^{t/l_{12}}-1\right)\left(l_{10}^2+l_{12}^2\right) \Big/\left\{(\lambda+2\mu)\left[l_{11}\left(e^{t/l_{11}}+1\right)\left(e^{t/l_{12}}-1\right)\left(l_{10}^2+l_{12}^2\right)^2-l_{12}\left(e^{t/l_{11}}-1\right)\left(e^{t/l_{12}}+1\right)\left(l_{10}^2+l_{11}^2\right)^2\right]\right\}, \tag{37a}$$

$$C_3=-C_4=b_0l_{12}^2e^{t/(2l_{12})}\left(e^{t/l_{11}}-1\right)\left(l_{10}^2+l_{11}^2\right) \Big/\left\{(\lambda+2\mu)\left[l_{11}\left(e^{t/l_{11}}+1\right)\left(e^{t/l_{12}}-1\right)\left(l_{10}^2+l_{12}^2\right)^2-l_{12}\left(e^{t/l_{11}}-1\right)\left(e^{t/l_{12}}+1\right)\left(l_{10}^2+l_{11}^2\right)^2\right]\right\}, \tag{37b}$$

leading to the following form of the displacement field

$$u_1=2C_1\sinh\frac{x_1}{l_{11}}+2C_3\sinh\frac{x_1}{l_{12}}. \tag{38}$$

It is interesting to note that the additional parameter, b_0 has appeared in Eqs. (37) since the surface effect is of importance. While in the analysis related to the bulk, which was discussed in the previous section, b_0 was absent.

In fact, as it will be shown in the remainder of this section, there is a relation between b_0 and the surface energy. To this end, consider the total strain energy, $\mathcal{W}$ for a body occupying volume V and enclosed by a smooth surface S

$$\mathcal{W}=\frac{1}{2}\int_V\left(\overset{1}{\boldsymbol{\tau}}:\nabla\mathbf{u}+\overset{2}{\boldsymbol{\tau}}:\nabla\nabla\mathbf{u}+\overset{3}{\boldsymbol{\tau}}::\nabla\nabla\nabla\mathbf{u}+b_0\nabla^2\nabla.\mathbf{u}\right)dV =\frac{1}{2}\int_V\mathbf{f}.\mathbf{u}dV+\frac{1}{2}\int_S\left(\overset{1}{\mathbf{t}}.\mathbf{u}+\overset{2}{\mathbf{t}}.D\mathbf{u}+\overset{3}{\mathbf{t}}.D^2\mathbf{u}+b_0\mathbf{n}.\nabla\nabla.\mathbf{u}\right)dS, \tag{39}$$

where $\overset{1}{\boldsymbol{\tau}}$, $\overset{2}{\boldsymbol{\tau}}$, and $\overset{3}{\boldsymbol{\tau}}$ are the stress tensors, $\overset{1}{\mathbf{t}}$, $\overset{2}{\mathbf{t}}$, and $\overset{3}{\mathbf{t}}$ are the applied surface tractions, and $D=\mathbf{n}.\nabla$ is the gradient in the direction normal to the surface. For the traction free film under consideration, in the absence of body forces, the expression for the total strain energy reduces to

$$\mathcal{W}=\frac{b_0}{2}\int_S\mathbf{n}.\nabla\nabla.\mathbf{u}dS. \tag{40}$$

The surface energy, γ is defined as the energy required for creation of one unit area of new surface and thus

$$\gamma=\frac{\mathcal{W}}{2A}=\frac{b_0}{4}\frac{d^2u_1}{dx_1^2}\Big|_{x_1=-t/2}^{x_1=t/2} =\frac{b_0^2\left(l_{11}^2-l_{12}^2\right)/(2(\lambda+2\mu))}{l_{11}\left(l_{10}^2+l_{12}^2\right)^2/\tanh\frac{t}{2l_{11}}-l_{12}\left(l_{10}^2+l_{11}^2\right)^2/\tanh\frac{t}{2l_{12}}}. \tag{41}$$

Note that γ has dimension of force per length, i.e., $[F/L]$, and l_{10} and b_0 have dimensions of $[L]$ and $[F]$, respectively. Appearance of b_0 and l_{10} in the formulations which are laid down in this section is a manifestation of the consideration of surface effects in the film. Moreover, as it is observed, b_0 has the same dimension as the cohesive force; Mindlin (1965) refers to b_0 as the "modulus of cohesion". It is interesting to note that the surface energy depends on the film thickness, however, as t becomes sufficiently large as compared to the bulk characteristic lengths, l_{11} and l_{12} such that $\tanh t/(2l_{11})$ and $\tanh t/(2l_{12})\to 1$, then the surface energy becomes independent of t and the surface energy expression given by Mindlin (1965) will be recovered. The dependence on t is the phenomenon of size effect captured by the second strain gradient elasticity in the free standing film problem.

A piece of useful information which would be of importance in ab initio calculations of the additional parameters (Section 4) is the exact expression for the change in the thickness of the film, Δt under the influence of its surfaces

$$\Delta t=\int_{-t/2}^{t/2}\frac{du_1}{dx_1}dx_1=-\frac{4l_{10}^2\gamma}{b_0}. \tag{42}$$

4. Determination of the surface energy and atomic force constants via ab initio simulation of the bulk and thin film

In this section, as a case study, the atomic force constants of bulk Al with face-centered cubic structure are evaluated using the ab initio calculations based on DFT. It will be shown that the atomic force constants are equivalent to the components of the Hessian matrix of the energy function of the material; Hessian matrix is defined as the second derivative of the total energy with respect to the atomic positions. Moreover, the surface characteristics

of Al such as surface energy is computed by simulation of the Al thin film via the first principles. In addition to the surface energy, the change in the film thickness caused by the surface effect is numerically determined through the ab initio calculations. Subsequently, utilizing the above-mentioned first principles numerical results, the Lamé and additional constants associated to the second strain gradient theory can be evaluated.

Ab initio calculations have been performed using the ab initio total-energy and molecular-dynamics program Vienna Ab initio Simulation Program (VASP) (Kresse and Hafner, 1993; Kresse and Hafner, 1994a; Kresse and Furthmüller, 1996a,b) which is based on DFT (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) and incorporates plane-wave basis set with ultra-soft pseudopotentials (Kresse and Hafner, 1994b). The kinetic energy cutoff for the plane-wave expansion is considered to be 320 eV. The grid in the first Brillouin zone is selected according to the Monkhorst–Pack (Monkhorst and Pack, 1976) scheme and the exchange–correlation energy is evaluated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof potential (PBE) revised for solids (Perdew et al., 2008).

The components of the Hessian matrix of the crystal energy due to the atoms $\mathbf{l}$ and $\mathbf{l}'$ are determined by employing central difference to the induced forces on each ion (each ion is displaced along each of its degrees of freedom separately and the effective force on each nucleus is determined numerically)

$$H_{ij}^{(\mathbf{l},\mathbf{l}')}=\left(\frac{\partial^2 E}{\partial r_i^{(\mathbf{l})}\partial r_j^{(\mathbf{l}')}}\right)_{\mathbf{r}^{(\mathbf{l})}=\mathbf{a}^{(\mathbf{l})}}\approx-\frac{F_j^{(\mathbf{l}')}\left(+\delta r_i^{(\mathbf{l})}\right)-F_j^{(\mathbf{l}')}\left(-\delta r_i^{(\mathbf{l})}\right)}{2\delta r_i^{(\mathbf{l})}},\tag{43}$$

where $F_j^{(\mathbf{l}')}\left(+\delta r_i^{(\mathbf{l})}\right)$ is the j^{th} component of the force exerted on the atom $\mathbf{l}'$ when the atom $\mathbf{l}$ is given an infinitesimal displacement $\delta r_i^{(\mathbf{l})}$ in the i^{th} direction. With due attention to the definition of $\mathbf{r}^{(\mathbf{l})}$ in Eq. (7), it is readily observed that

$$\left(\frac{\partial^2 E}{\partial r_i^{(\mathbf{l})}\partial r_j^{(\mathbf{l}')}}\right)_{\mathbf{r}^{(\mathbf{l})}=\mathbf{a}^{(\mathbf{l})}}=\left(\frac{\partial^2 E}{\partial u_i^{(\mathbf{l})}\partial u_j^{(\mathbf{l}')}}\right)_{\mathbf{u}^{(\mathbf{l})}=0},\tag{44}$$

and consequently, the components of the Hessian matrix of crystal energy are equivalent with the corresponding atomic force constants

$$H_{ij}^{(\mathbf{l},\mathbf{l}')}=U_{ij}^{(\mathbf{l},\mathbf{l}')}.\tag{45}$$

The components of the fourth order elastic moduli for Al are evaluated employing the relations (22a) and (28a). The numerical results for the Al elastic moduli C_{1111}, C_{1212}, and C_{1122} are compared with some experimentally and computationally obtained results available in the literature, Table 3. Lincoln et al. (1967) have evaluated the Al elastic constants using a central-force model via the Morse potential. In this model, the elastic constants obey the Cauchy relation $C_{1122}=C_{1212}$. However, the results obtained by current calculations which are in reasonable accordance with the experimental ones show that the Al fourth order elastic moduli do not obey the Cauchy relations.

Table 3
Fourth order elastic moduli of Al compared with some experimental and computational results available in the literature.

Al	$C_{1111}\left(\text{eV/Å}^3\right)$	$C_{1122}\left(\text{eV/Å}^3\right)$	$C_{1212}\left(\text{eV/Å}^3\right)$
Present work	0.66	0.38	0.23
Central-force model (Lincoln et al., 1967)	0.56	0.4	0.4
Exp. (Ho and Ruoff, 1969)	0.67	0.38	0.18
Exp. (Huntington, 1958)	0.68	0.38	0.18

The numerical results for the Hessian matrix components along with the relations (22), (28), (45), and the data included in Tables 1 and 2, result in the following relations

$$a_1=4a_3,\tag{46a}$$

$$c_1=\frac{3a_1}{4}-0.0791\quad\text{eV/Å},\tag{46b}$$

$$b_1=0.0015\quad\text{eV.Å}.\tag{46c}$$

Using the obtained values and relations, the characteristic lengths of Al crystal are evaluated as below

$$l_{11}=0.946\quad\text{Å},\tag{47a}$$

$$l_{12}=0.216\quad\text{Å},\tag{47b}$$

$$l_{21}=0.809\quad\text{Å},\tag{47c}$$

$$l_{22}=0.182\quad\text{Å}.\tag{47d}$$

In summary, the eighteen additional parameters are reduced to seven, consisting of a_1, a_3, c_1, b_1, and b_0 via Eqs. (29) and two Lamé constants. By ab initio analysis for the bulk, as shown by Eqs. (46), the mentioned five parameters are reduced to only two parameters c_1 and b_0. Moreover, by utilizing Eqs. (46) and (47), we can readily calculate all four characteristic lengths, l_{11}, l_{12}, l_{21}, and l_{22} from Eqs. (31). Finally, the surface characteristic length, l_{10} can be obtained by simply inserting $\bar{c}=5c_1$ (c_1 is obtained from the surface analysis) and λ and μ (obtained from the bulk analysis) into Eq. (36). It should be emphasized that the bulk characteristic lengths, l_{11}, l_{12}, l_{21}, and l_{22} are physically different entity as compared to the surface characteristic length, l_{10} and there is no relation between these entities, whatsoever.

Note that Lamé constants and the characteristic lengths are the sole material parameters involved in the second gradient equilibrium equations, (30) for the bulk. Hence, without consideration of the surface effect, all the additional constants cannot be determined and two more equations are required to calculate the modulus of cohesion, b_0 and surface characteristic length, l_{10}. To obtain these parameters, one can take advantage of the concept of surface energy which is an important surface parameter as well as accounting for the change in the thin-film thickness. As derived in Section 3, these two parameters are expressed in terms of b_0, Lamé constants, material characteristic lengths, l_{10}, l_{11}, and l_{12}, and film thickness, t via Eqs. (41) and (42). For sufficiently large values of the film thickness, t in comparison with l_{11} and l_{12}, the surface energy would be unaffected by the film thickness. In our ab initio DFT calculations, the values of γ and Δt are obtained for various film thicknesses; subsequently, b_0 and l_{10} are calculated using the analytical expressions (41) and (42). The threshold value of t for which γ, Δt, b_0, and l_{10} would no longer vary with increasing t is obtained; the threshold value of t corresponds to the film thickness beyond which the two free surfaces of the film have no interactions. The Al(001) thin films of different thicknesses are simulated employing VASP as described earlier. In view of the periodic boundary conditions which are employed to obtain the unit cell energy levels, a sufficient number of vacuum layers should be inserted along the direction [001] to eliminate the interaction of the subsequent surfaces in the simulation. The first principles calculations are performed for the Al(001) films of thicknesses 9, 11, 13, 15, and 17 atomic layers. The ab initio results for surface energy, γ and the ratio of the thickness change, $\frac{\Delta t}{t}$ together with the analytical values for the modulus of cohesion, b_0, surface characteristic length, l_{10}, and parameter c_1 are summarized in Table 4. For $t=9$ atomic layers, $l_{11}=0.946$ Å yields $\tanh(t/2l_{11})=1.0$, implying that for films thicker than 9 atomic layers, the pertinent surface energy, according to Eq. (41), becomes independent of the film thickness. From the ab initio DFT results displayed in Table 4, it is observed that the discrepancies between the surface

Table 4
Surface energy and the ratio of the change of the film thickness to its initial thickness evaluated for Al(001) films of different thicknesses together with the corresponding calculated values for b_0, l_{10}, and c_1.

t	No. of atoms	$\gamma\ \left(\mathrm{eV/\AA^2}\right)$	$\frac{\Delta t}{t}$	b_0 (eV/Å)	l_{10} (Å)	c_1 (eV/Å)
9-layer	36	0.0477	0.05	0.110	$0.668i$	−0.075
11-layer	44	0.0499	0.04	0.119	$0.695i$	−0.081
13-layer	52	0.0492	0.04	0.088	$0.645i$	−0.070
15-layer	60	0.0485	0.04	0.061	$0.608i$	−0.062
17-layer	68	0.0507	0.04	0.052	$0.596i$	−0.060

energies for two consecutive thicknesses are about 4% and remains nearly unchanged with increasing thickness. The observed discrepancy is not due to the issue that the film thickness is not thick enough, but it is because of the accuracy of the ab initio calculations. Therefore, from our analytical solution as well as the ab initio calculations, it is inferred that $t=9$ atomic layers is a reasonable threshold value for the film thickness.

Fiolhais et al. (2003) employed DFT with various approximations for the exchange and correlation energy to study the surface energy associated with different Al surfaces. In particular, for the Al(001) surface energy, they reported the values of 0.058, 0.066, and 0.094 $\mathrm{eV/\AA^2}$ which correspond to the second-order perturbative results using Heine-Abarenkov pseudopotential with slabs of 6 and 7 atomic layers, the stabilized jellium with GGA-PBE after applying the corrugation factor, and all-electron calculations with CRYSTAL98 code for slabs of 1 to 10 layer(s), respectively. As far as the experimental works are concerned, Tyson and Miller (1977) have reported the value of 0.073 $\mathrm{eV/\AA^2}$, for the surface energy without mentioning the correspondent surface. One may conclude that in addition to the employed potentials, there are various parameters that can affect the final results. Thus, generally speaking, all the mentioned results and the values given in Table 4 are of the same order and, commonly, are considered to be in a reasonable agreement.

5. Conclusion

In this article, the modulus of cohesion and other material constants associated to the second strain gradient elasticity, which is a suitable method for consideration of the surface effects, are evaluated via the first principles calculations combined with the lattice dynamics. In one hand, the second strain gradient theory is applied to the infinitely extended bulk material of isotropic symmetry and subsequently merged with the lattice dynamics to derive the relations between the atomic force constants and Lamé and additional constants. On the other hand, the second strain gradient is employed to scrutinize the surface effects in the free standing film, a manifestation of which is the derivation of the expressions for the surface parameters such as the surface energy and change in the film thickness in terms of the Lamé and additional constants. By employing the DFT simulations of both the bulk and thin film, the numerical values of, respectively, the bulk atomic force constants and the surface energy as well as the change in the film thickness are obtained. Then the Lamé and additional constants pertinent to the second strain gradient elasticity are evaluated analytically. Through this analysis, an analytical expression for surface energy is derived which depends on the film thickness, modulus of cohesion, Lamé constants, and the material characteristic lengths. It is readily observed that the thickness dependency of the film surface energy vanishes for sufficiently thick films.

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